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Concentration Characteristics and Health Risk Assessment of Heavy Metals in the Water of Nandong Underground River Watershed, China

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Abstract: Rejected material from human activities had great impact on water quality that result in limit water usability for domestic purposes. Usually, wastes discharged from people activities or earth background usually consist of undesirable concentrations of soluble chemicals that infiltrate into the surrounding water, and then constitute health risk to local residents. In order to investigate the concentration characteristics and health risk for the populace in Nandong Underground River Watershed (NURW), eleven common heavy metals in the water body analysis were conducted. Health risk assessment (HRA) model was taken to analyze eleven heavy metals of 84 water samples from surface and underground waters in NURW (36 samples underground water and 48 samples surface water). Our results showed that the heavy metals concentration order was Fe > Al > Mn > Zn > As > Cd > Pb > Cr > Ni > Cu > Hg. Correlation analysis indicates that these eleven metal elements have certain similarity on material source and migration transformation way. The health risks for local residents exposed to metal elements in the water of NURW mainly from carcinogenic risk (10^{-6} ～10^{-4} a^{-1}) through drinking way, and the health risk of heavy metals exposed to children through drinking way was much higher than adults. The maximum exposing health risks of Cr in both underground and surface water were higher than the recommendation standard (5.0×10^{-5} a^{-1}) from ICRP, and all the values over the standard (5.0×10^{-6} a^{-1}) recommended by the Swedish Environmental Protection Agency and the Dutch Ministry of Construction and Environment and the British Royal Society. The results of health risk assessment shows that Cr in the water of NURW was the mainly source of carcinogenic risk for the local residents, following by Cd and As. Consequently, it is necessary to control the three carcinogenic metals when the water was used as drinking water resource.

Keywords: Concentration Characteristics; Health Risk Assessment; Heavy Metals; Nandong; Underground River Watershed

1. Introduction

Heavy metals are widely distributed in various environmental backgrounds and have characteristics of permanence, carcinogenicity, biomagnification and biocondensation etc. which easy to cause serious environment pollution and lead to negative effects on human health. Some heavy metals are essential for constitute the living organism's body and promoting metabolism, while they have been reported to be toxic for human body when concentrations were surplus [**1**,**2**,**3**,**4**]. Representative studies embody in the reports of arsenic element, which have been revealed that arsenic was well-known for its toxicity in water, carcinogenicity and has the potential to cause damnification of the nervous system, liver and skin [**5**,**6**]. Typical research such as Ciner et al. found that due to the mass daily drinking of arsenic-contaminated water, children and adults in central Turkey were suffered from exposed to carcinogenic risks of arsenic [**4**]. In China, Luo et al. assessed the potential of element dispersion and health risks associated with potentially toxic elements in the soil-water-plant system in the Xiangtan manganese mine, and found severe contamination of the tripartite system for Mn, Cd and Pb, and revealed that these three heavy metals can transferred from the soil-water-plant system to human body through the food chain [**7**]. Furthermore, studies have shown that those so-called non-carcinogenic metals such as Al, Mn，Cu, Fe and Zn yet have potential health risk if excess accumulated in human bodies [**11**,**12**].

With the rapid development of socio-economy, industry and urbanization in recent decades, many countries have emerged serious environment pollution and then threatened to people’s health [**8**,**9**]. Get rid of heavy metals from industrial, agriculture, resident life and earth background was popularly believed can increased the levels of heavy metals in water [**8**]. Nature and human activities often affect the water quality within a certain region. Natural factors such as topography feature, hydrogeological condition, wealthy soil layer and geological background can lead to heavy metals contamination of surface water and groundwater [**10**]. Furthermore, anthropogenic activities such as industrial sewage discharge, agricultural contamination and domestic litter cause water pollution, especially serious in those densely-populated and industrial developed areas such as Ota Industrial area in Ogun State, Nigeria [**13**]. Similarly, regions that over-mining areas have caused mass heavy metals discharge to the water body and bring health threat to the local residents, which have got major attention from the local authorities [**7**, **14**].

The Nandong Underground River Watershed (NURW) is one of the four ultra-large groundwater river watersheds in Southwest of China [**15**,**16**], which is a typical karst aquifer structure and groundwater system that has long served as the water resource for industry, domestic and agriculture usage. In recent years, the human activities have not only degraded the ecological environment, but also made some water bodies polluted and affected the water quality [**17**,**18**]. Since has the special geological structure with high altitude mountain in upstream recharge areas, series faulted basins in midstream runoff-discharge areas, and has the only one groundwater debouchure in the low altitude area, studied has been revealed that mass NO_3^- and SO_4^{2-} released from human activities in the middle and upstream recharge-runoff areas of NURW are dissolved in surface water and groundwater and reach levels of harmful contents at the outlet of the underground rive [**19**].

However, it was not clear that the water quality and potential health risk of heavy metal elements in NURW by far. This paper researched 11 common heavy metals (Al, Cu, Pb, Zn, Cr, Cd, Ni, Mn, As, Fe and Hg) in the surface water and groundwater in NURW. We selected representative surface water and groundwater points in the watershed and take samples once monthly during a whole year from 2021 to 2022, test the above 11 common heavy metals concentrations in the water samples from NURW, next analyzed distribution, pollution status, and dynamic change characteristics of these 11 common heavy metals during the study period. Furthermore, we used HRA model recommended by the United States Environmental Protection Agency (USEPA) to assess the health risk to local residents in NURW [**23**,**24**]. The results of this study will help in policy makers know the water quality of NURW and formulate scientific and reasonable regulations on the use of the waters for sustainable development goal in NURW.

2. Description of Study Area

The study area, Nandong Underground River Watershed is located at the southeast of the Yun-Gui Plateau in Yunnan Province, China (**Figure. 1**), with the whole catchments area about 1684 km². The climate conditions belong to subtropical monsoon with annual precipitation of 830 mm and mean air temperature of 19.8 °C [**17**]. In 2021, the total population in the area was about 0.45 million, 60% of them is living in the rural and engaging in agricultural activities. A third of the gross domestic product (GDP) was from agricultural output value. Since has the significant characteristic of karst faulted basin, the whole watershed present basin-mountain coexistence topographic feature, and has special geological structure with high altitude mountain in upstream recharge areas, series faulted basins in midstream to runoff-discharge areas. Since has the big elevation difference, the mountains in upstream recharge areas are high 2200-2700 m, while drop to about 1300 m in midstream runoff-discharge basins areas and low to 1000 m at the outlet of Nandong underground rive. Altogether, the underground and surface water flow from the surrounding mountains to the basins, the surface water system is underdeveloped and only have a few small rives pass through the basins area, all of them flow together in one point discharge out at Xiaguan Kou (**Figure. 1**). The outlet of groundwater is at Nandong Kou and is the only discharge point of the whole watershed. Hence, materials that were released from geological background or human activities dissolve in the water and most of them were carried to the total outlet of surface water and groundwater, it provides the ideal conditions for this study.

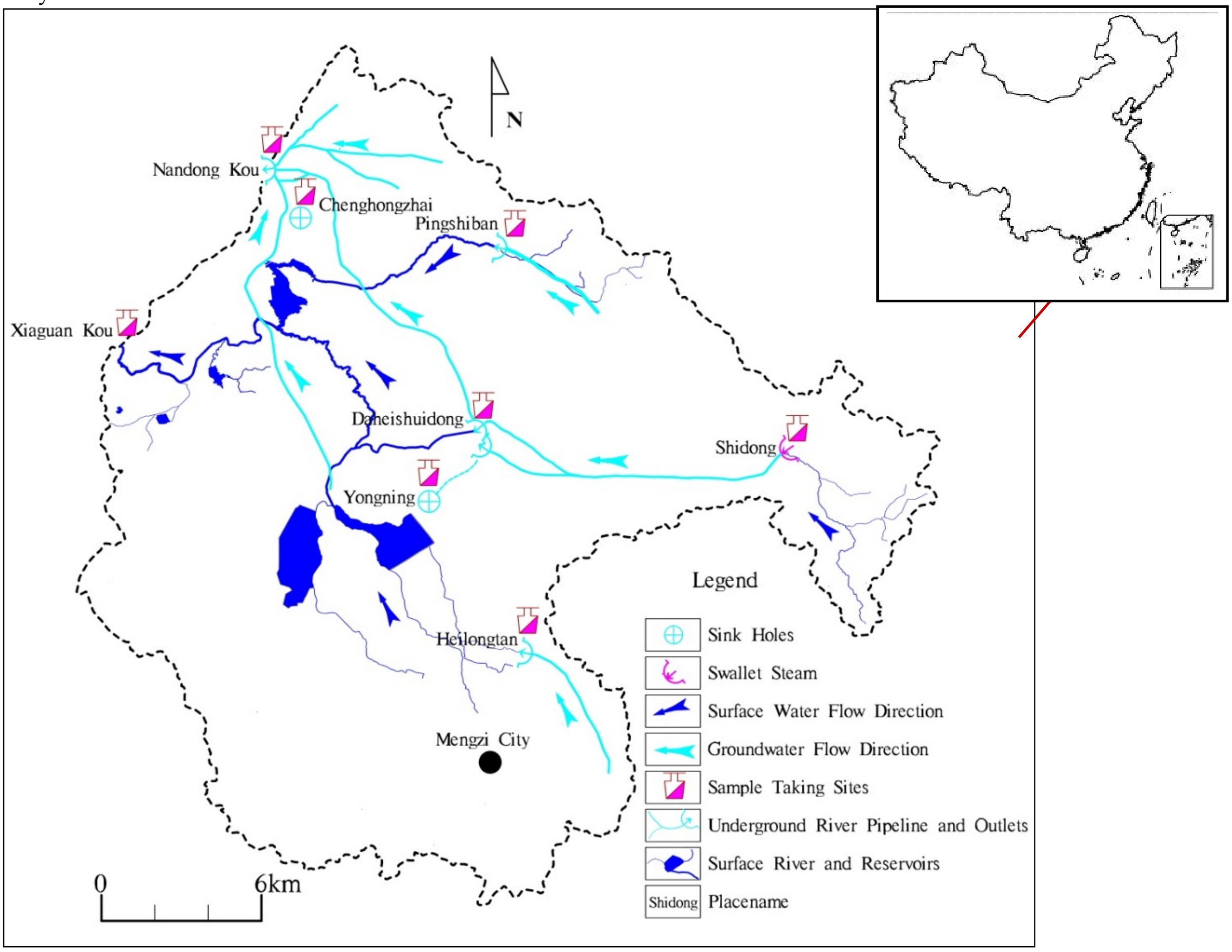


Figure 1. Location of study area, surface-underground water system of Nandong Undeground River Watershed and sampling sites in our study.

3. Materials and Methods

3.1. Samples collection and test

In order to comprehensive study the whole watershed, we selected seven typical sampling points that distribute in difference place in NURW, in these sampling points, include sink holes, swallet steams，surface river sections and groundwater outlets, the sampling sites were marked in **Fig.1**. Samples were taken once per month from 2021 to 2022. Altogether 84 samples were collected throughout the whole year. During took water sample, collected the conventional ions of water chemistry in polyethylene bottles. Rinsed all empty bottles with deionized water and used original sample water clean the empty bottles three times before taking samples, filter the original water samples with 0.45 μm microporous filter and bottling, each group of sample take 1000 ml water and divided into two 500 ml sampling bottles, titrate 2 ml HNO_3 (1:1) into each bottle to stabilize the heavy metals in the water and seal up each bottle by membrane in field scene and stored at 4 °C ice box and transported to laboratory to test the elements concentrations as soon as possible. Conventional chemical indicators such as DO, pH，Eh and electrical conductivity were tested by multi-parameter instrument on the field spot. Concentrations of the 11 heavy metal elements of all samples were test in Karst Geology and Resources Environment Testing Center, Department of Natural Resources, China. Al, Cu, Pb, Zn, Cr, Cd, Ni, Mn, As and Hg were tested by inductively-coupled plasma mass spectrometer (ICP-MS), Fe element was tested by full universal straight read plasma spectrometer (IRIS Intrepid Ⅱ XSP). All indicators (elements) from every sample were tested three times and take the mean values as the final detection data. Blank samples were also controls during the test proceeding, the standard deviations of all the results of all samples were kept less than 5%.

3.2. Health risk assessment model

3.2.1. Average daily exposure dose

In general, heavy metals in the water into human body through drinking or skin contact, more than 90% pollutants enter human body through these two ways [**20**,**21**]. As a common of pollutant, metals can be divided into carinogenic and non-carinogenic health risk after entering the human body [**22**]. The health risk assessment model recommended by the US EPA for hazardous substances in water was used to assess the health risk of adults and children under these two exposure models [**23**,**24**].

The average daily dose from exposure to metals through drinking water defined by:

$$\mathrm{ADD}_i = \frac{C_w \cdot \mathrm{IR} \cdot \mathrm{ED} \cdot \mathrm{EF}}{\mathrm{BW} \cdot \mathrm{AT}} \tag{1}$$

The average daily dose from exposure to metals through skin contacting defined by:

$$\mathrm{ADD}_d = \frac{C_w \cdot \mathrm{SA} \cdot \mathrm{ET} \cdot \mathrm{ED} \cdot \mathrm{EF} \cdot \mathrm{CF} \cdot \mathrm{PC}}{\mathrm{BW} \cdot \mathrm{AT}} \tag{2}$$

Where ADD_i and ADD_d are the average daily dose per unit body weight of metal element W exposed through drinking water and skin contacting mg $(\mathrm{kg.d})^{-1}$; C_w is the average concentration of the metal element W, mg.L-1; IR is the average daily ingestion rate of human beings, and usually make 2.2 $\mathrm{L.d}^{-1}$ for adults and 1 L.d-1 for children [**25**]; ED is the exposure duration of the metal element W, with 70 a for carcinogenic metal elements and 35 a for non-carcinogenic metal elements [**25**]; EF is the exposure frequency of the metal element W, calculated in 365 $\mathrm{d.a}^{-1}$ [**26**]. BW is the body weight, the average weight of adults in Yunnan is 57.0 kg, and in the children is 23.8 kg [**25**]; AT is the average exposure time, the carcinogenic metal element is 25550 d (70 a), and the non- carcinogenic metal element is 12775 d (70 a) [**27**]. In formula (2), SA is the contact area between water and skin, 18000 cm^2 for adults and 8000 cm2 for children [**28**]; ET is the average daily exposure time, 0.633 $\mathrm{H.d}^{-1}$ for adults and 0.4167 H.d-1 for children [**25**]; CF is the volume conversion factor, $\mathrm{mL{\cdot}(cm^3)^{-1}}$. PC is the element metals permeability coefficient to human skin when contacting, $\mathrm{cm{\cdot}h^{-1}}$.

3.2.2 Health risk assessment

Considering metals elements have different carcinogenic intensities when they exposure to the crowd, according to the International Agency for Research on Cancer (IARC) and the World Health Organization (WHO), we conducted health risk assessment of As, Cr, Cd as chemical carcinogenic metal elements, and conducted health risk assessment of Al, Cu, Pb, Zn, Fe, Ni, Mn, Hg as chemical non-carcinogenic metal elements.

The health risk assessment formula for chemical carcinogenic metal elements in water is defined by:

$$R_n = \frac{\mathrm{ADD} \cdot \mathrm{SF}}{L} \tag{3}$$

The health risk assessment formula for chemical non-carcinogenic metal elements in water is defined by:

$$R_n = \frac{\mathrm{ADD}}{\mathrm{RfD} \cdot L} \tag{4}$$

Where R_n is the health risks of chemical carcinogenic and non-carcinogenic metal element, a^{-1} in the water; ADD is the average daily dose per unit body weight of metal element W exposed through drinking water or skin contacting mg $(kg.d)^{-1}$; SF is the slope factor of the chemical carcinogenic metal W through drinking or skin contacting water, $(kg.d).mg^{-1}$. L is the average human lifetime, which in Yunnan residents is 70 a [**11**]. RfD is the reference dose of daily taken of a chemical non-carcinogenic metal element W through drinking or skin contacting water, mg. $(kg.d)^{-1}$. The parameters values of PC, SF and RfD are shown in **Table 1**.

Table 1. the Values of parameters related to health risk assessment.

Metal		PC (10^{-3}/cm·h^{-1})	SF/(kg·d)·mg^{-1}		RfD/mg·(kg·d)$^{-1}$	
			Drinking Water	Skin Penetration	Drinking Water	Skin Penetration
Carcinogenic	As	1.8	1.5	3.66		
	Cr	2	41	41		
	Cd	1	6.1	6.1		
Non-carcinogenic	Al	10			0.14	0.14
	Cu	0.6			0.04	0.012
	Pb	0.004			0.0014	0.00042
	Zn	0.6			0.3	0.01
	Fe	0.1			0.3	0.045
	Ni	0.1			0.02	0.0054
	Mn	0.1			0.046	0.0018
	Hg	1.8			0.0003	0.0003

*No reference standard value.

3.2.3. Total health risk assessment

In this study, we use HRA model recommended by the United States Environmental Protection Agency (USEPA) to assess the health risk to human [**23**,**24**]. We hypothesized that the health risk exposed to heavy metals in water has a cumulative relationship, so the total health risk of multi-elements Rt is defined by equation below:

$$R_t = \sum R = R_i^c + R_i^n + R_d^c + R_d^n \qquad (5)$$

3.3 Mathematical statistics and analytical methods

In this study, we use Excel 2013 to sort, statistic and calculate the original test data; Use SPSS Statistics 22 to perform correlation analysis; Use MapGis 6.7 to draw the distribution map of sampling points in our study area (NURW); Use Origin 9.1 to draw concentration of 11 metal elements changing diagrams and those health risk figures of exposure to the local residents.

4. Results and Discussion

4.1. Concentration characteristics of heavy metal elements in the water

Concentrations of the 11 heavy metal elements Al, Cu, Pb, Zn, Fe, Cr, Cd, Ni, Mn, As and Hg are shown in **Table 2**. The average concentrations of 11 heavy metal elements in the water samples in NURW show the order of Fe> Al >Mn >Zn> As >Cd >Pb >Cr> Ni> Cu >Hg. Among these elements, Fe, Al and Mn show the higher concentrations than the other 8 elements, and reach 10^{-2} μg·L^{-1} range. According to the limit values of Grade Ⅲ water specifies in *Standard for Surface Water Environmental*

Quality (GB 3838-2002), Standard for Groundwater Quality (GB/T 148-2017), the *Standard for Drinking Water Quality (GB 5749-2006)* and the US EPA drinking water quality standard [**29**,**30**,**31**,**32**,**33**], the concentrations of Al, Pb, Zn, Fe, Cd, Mn, As and Hg from our water samples exceeded all the three standard limitations mentioned above. Maximum concentrations of all the exceeded standard limitations elements reached 26.37, 12.40, 1.31, 25.97, 12.20, 20.34, 5.47 and 9.40 multiple of standards respectively. Obviously, Hg, Al and Fe are the three elements that exceeded standard limitation highest in the research area waters, and the maximum values of these three elements concentrations show more than 20 times exceed standard. Therefore, more attention must be paid special for Hg, Al, Fe and Mn elements before used. In contrast with the standard of USEPA and WHO, most water quality index values in China are less than or equal to standard limits of America and International, only Cd (5 $\mu g \cdot L^{-1}$) standard limits in China is higher than WHO (3 $\mu g \cdot L^{-1}$). Consequently, from the perspective of international indicators, Cd in our study area water also needs to attract attention.

According to the previous study, the variation coefficient for metal elements can reflect the influent degree of space-time scale on metal elements concentrations [**34**], and it is generally assumed that variation coefficients less than 0.2 is considered to be in low variation level, 0.2 to 0.5 is in medium variation level, 0.5 to 1.0 is in large variation level, and reach the strong variation level when the coefficients larger than 1.0 [35]. It can be seen from **Table 2** that the variation coefficient of 11 metal elements in our study area were in the order of Pb > Cd > Zn > Mn > Fe > Al > Cu > As > Ni > Hg > Cr， there are eight elements which variation coefficients are larger than 1.0, variation coefficients of Cr, Ni and Hg change between 0.5 to 1.0. The results indicated that the concentration distributions of 11 metal elements taken from the seven sampling points in NURW have greatly spatiotemporal distribution different during our study period. The main reason is water system circle more intense and changeable in NURW, seasonal changing of human activities intensity, mineral composition of aquifer are complex and easily affected by seasonal climate changes etc.

Table 2. Concentrations of metals in the water of Nandong Groundwater River Watershed ($\mu g \cdot L^{-1}$).

Metals *n*=84	**Scope**	**Average**	**Standard Deviation**	**Variation Coefficient**	**Exceed Standard limitation (%)**
Al	9.90~5274.00	440.04	913.09	2.08	38.10
Cu	nd~26.70	2.34	4.75	2.03	0
Pb	nd~124.00	3.62	15.43	4.26	2.38
Zn	nd~1311.00	82.39	211.24	2.56	1.19
Fe	nd~7790.00	486.83	1127.61	2.32	26.19
Cr	1.10~10.70	3.47	2.08	0.60	0
Cd	nd~61.00	3.63	10.34	2.85	7.14
Ni	0.78~13.90	2.99	2.22	0.74	0
Mn	2.44~2035.00	113.13	276.85	2.45	15.48
As	nd~54.70	6.13	8.01	1.31	17.86
Hg	nd~0.94	0.41	0.26	0.63	40.48

Metals *n*=84	**China**			**US EPA**	**WHO**
	Drinking Water (Limits)	Surface Water（III）	Ground Water（III）	Drinking Water	Drinking Water
Al	200	–	200	–	200
Cu	1000	1000	1000	1300	2000
Pb	10	50	10	15	10

Zn	1000	1000	1000	–	–
Fe	300	–	300	–	300
Cr	50	50	50	100	50
Cd	5	5	5	5	3
Ni	20	–	20	–	70
Mn	100	100	100	–	400
As	10	50	10	10	10
Hg	1	0.1	1		

*nd means not detected, –means no corresponding reference value.

Fig 1 shows the distributions and dynamic changing characteristic of metal elements in the surface water and groundwater from January to December. From the spatial distribution, we can see that Zn, Cr, Cd and Ni elements in the groundwater samples are higher than that in the surface water samples in most months during the study period, while As shows the opposite characteristic. From the time scale, element variation amplitudes in the groundwater were larger than surface water. The concentration of Al, Cu, Pb, Zn, Fe, Cr, Ni and Hg in all water samples present the similar trend of time changing, while Zn and Cd elements present the opposite changing trend. Special attention should be paid to Al, Pb, Zn, Fe, Cd, Mn, As and Hg during they have high concentrations and exceed standard limitation period. Such as Al element show high concentration from January to March in surface water and it shows high concentration from June to September in groundwater. This can helps the local residents take this issue seriously and try to avoid risk when they utilizing these waters.

4.2. Correlation analysis

The correlation matrix for the 11 heavy metals and pH in the water samples is shown in **Table 3**. As shown in the table, all of the correlations of water pH with each element were not significant ($p > 0.05$). Which indicate that pH impact to the concentration distributions of metal elements was not obvious, the reason is due to most pH from the water samples in the study area are 6.84~7.96，and the coefficient of variation was only 0.02, which has not change much for the whole year. There are significant positive correlations ($p < 0.01$) occurred between each other in the Al, Cu, Pb, Fe, Cr, Ni and Mn elements. Zn shows significant positive correlations with Cd, Ni, Mn, Cu and Pb at $p < 0.01$, and shows significant positive correlation with Al at $p < 0.05$. As shows significant positive correlations with Cu, Fe and Mn at $p < 0.01$, and shows significant positive correlations with Pb at $p < 0.05$. The results indicate that these metal elements have certain similarity on material source and migration transformation [**28**, **36**]. Besides, Hg showed significant negative correlation with Cr at $p < 0.01$ and showed significant negative correlations with Ni at $p < 0.05$. This illustrates that Hg distinguished on original source and migration transformation sharply from Cr and Ni elements.

Table 3. Pearson correlation matrix for metals and pH in the water samples.

n=84	pH	Al	Cu	Pb	Zn	Fe	Cr	Cd	Ni	Mn	As	Hg
pH	1.000	0.045	0.040	0.134	−0.022	0.032	0.179	−0.070	0.109	0.024	−0.041	−0.147
Al		1.000	0.746^{**}	0.579^{**}	0.240^{*}	0.929^{**}	0.632^{**}	0.037	0.916^{**}	0.652^{**}	0.290^{**}	−0.201
Cu			1.000	0.756^{**}	0.692^{**}	0.700^{**}	0.479^{**}	0.171	0.805^{**}	0.920^{**}	0.282^{**}	−0.172
Pb				1.000	0.285^{**}	0.490^{**}	0.351^{**}	0.112	0.690^{**}	0.486^{**}	0.268^{*}	−0.103
Zn					1.000	0.166	0.210	0.469^{**}	0.327^{**}	0.757^{**}	0.060	0.016
Fe						1.000	0.641^{**}	0.014	0.836^{**}	0.659^{**}	0.447^{**}	−0.207
Cr							1.000	0.199	0.643^{**}	0.431^{**}	0.169	-0.292^{**}
Cd								1.000	0.095	0.141	0.032	0.297^{**}
Ni									1.000	0.657^{**}	0.206	-0.237^{*}

Mn		1.000	0.294**	−0.154
As			1.000	−0.014
Hg				1.000

* Significant at 0.05 level.

** Significant at 0.01 level.

4.3. Health risk assessment of heavy metals in the water

According to the heavy metals elements concentrations in our study area surface water and underground water, we used health risk assessment model to calculated annually per capita carinogenic and non-carinogenic health risk in Nandong Underground River Watershed (**Table 4**).

The health risk assessment of result by drinking water: the maximum of annually per capita carinogenic risk (10^{-6} ~ 10^{-4} a^{-1}) are higher than non-carinogenic health risk (10^{-11} ~ 10^{-8} a^{-1}) through drinking. The annual total health risk for children was much higher than adults caused by drinking water, this mainly attributed to children are more sensitive to the risk receptors than adults [**40**]. The maximum datum of carinogenic risks caused by the heavy metal elements in the water were show the order of Cr > Cd > As in groundwater and Cr > As > Cd in surface water. All the most significant risk of Cr （2.74×10^{-5} ~ $2.30\times10^{-4}a^{-1}$） in surface and underground water samples exceed the maximum acceptable risk value of 5.0×10^{-5} a^{-1} stipulated by the International Commission on Radiological Protection (ICRP) for children and adults [**41**,**42**,**43**]. Furthermore, carinogenic risk caused by Cr from underground water is lower than surface water. The most significant risk of Cd (2.32 ~ 1.95×10^{-4} a^{-1}) in underground water samples exceed the maximum acceptable risk value of 5.0×10^{-5} a^{-1} stipulated by the International Commission on Radiological Protection (ICRP) for children and adults. Fortunately, the most significant risk of Cd in the surface water does not constitute an obvious harm for children and adults. From the results we can see that the underground water in Nandong Watershed have some enrichment effects for Cd. In all of the water samples, only the most significant risk of As in the surface water that exposed to children exceed the maximum acceptable risk value of ICRP. Thereby, to avoid the potential carcinogenic risk for local residents, it needs to treat Cr, Cd and As in the water before using as the drinking water resource. The maximum datum of no-carinogenic risks caused by heavy metal elements in the water were in the order of Pb > Mn > Al > Fe > Zn > Hg > Ni > Cu in underground water samples and Al > Pb > Mn > Fe > Hg > Ni > Cu > Zn in surface water samples. From the results it can be seen that the no-carinogenic metal elements and the total health risk in our study are all lower than 5.0×10^{-5} a^{-1}. Consequently, there are no potential health risks for no-carinogenic metal elements in the water that was exposed to the local residents through drinking way, while carinogenic metal elements in the water are the mainly source of potential health risk for the local residents through drinking way.

The health risks result by skin penetration: All the 11 metal elements in our study present the maximum datum of annually per capita carinogenic risk (10^{-8} ~ 10^{-6} a^{-1}) higher than non-carinogenic health risk (10^{-13} ~ 10^{-9} a^{-1}) through skin penetration. Distinguishes from the results of drinking water, the average annual total health risk that caused by skin penetration was lower for children than for adult. Simultaneously, the health risk for the local residents exposed to metal elements in the water bodies of Nandong Underground River Watershed that caused by skin penetration are lower than by drinking way (lower 1 ~ 2 order of magnitudes). The most significant health risk for residents exposed to carcinogenic metal elements were in the order of Cr > Cd > As in underground water and Cr > As > Cd in surface water bodies. Exposing to no-carcinogenic metal elements were in the order of Al > Mn > Zn > Fe > Hg > Cu > Pb > Ni in underground water and Al > Mn > Fe > Hg >Zn > Cu > Pb > Ni in surface water bodies. Meanwhile, the annual total carinogenic and non-carinogenic health risk values for residents caused by skin penetration were concentrated of 10^{-6}-10^{-13}.a^{-1}, which was much lower than 5.0×10^{-5}.a^{-1}. Therefore, the 11 metal elements in water through skin penetration did not bring significant harm to local residents.

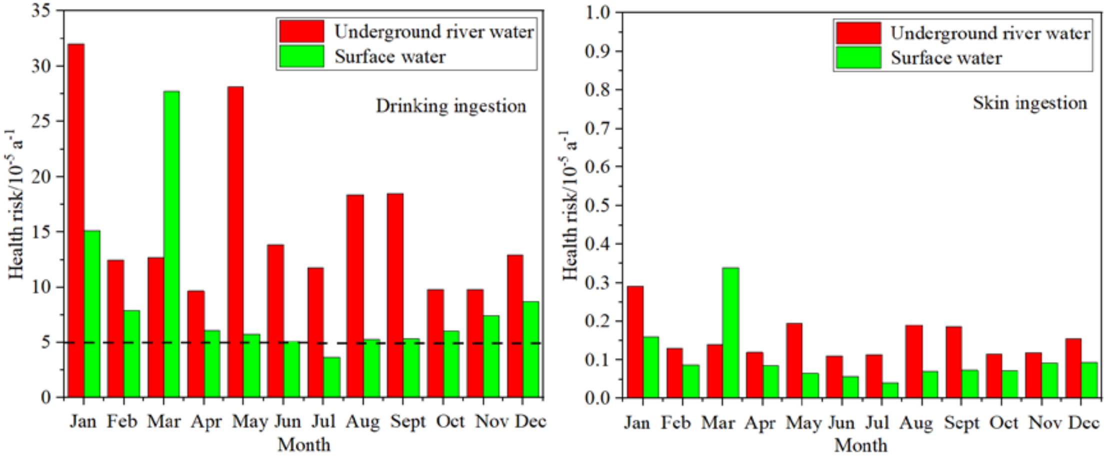
Table 4. Annually per capita health risks caused by metals in different types of water though drinking water and skin penetration, respectively (a^{-1}).

Exposure Way		**Metals**	**Groundwater**		**Surface Water**	
			Adults	Children	Adults	Children
Drinking Water	Carcinogenesis	As	/～1.93×10^{-5}	/～2.30×10^{-5}	6.91×10^{-7}～4.30×10^{-5}	8.24×10^{-7}～5.12×10^{-5}
		Cr	5.11×10^{-5}～2.30×10^{-4}	6.09×10^{-5}～2.74×10^{-4}	2.36×10^{-5}～2.30×10^{-4}	2.81×10^{-5}～2.74×10^{-4}
		Cd	/～1.95×10^{-4}	/～2.32×10^{-4}	/～4.67×10^{-6}	/～5.56×10^{-6}
	No-carcinogenesis	Al	4.53×10^{-11}～1.97×10^{-8}	5.39×10^{-11}～2.35×10^{-8}	3.70×10^{-11}～1.69×10^{-8}	4.41×10^{-11}～2.01×10^{-8}
		Cu	/～3.50×10^{-10}	/～4.16×10^{-10}	2.23×10^{-12}～2.70×10^{-10}	2.65×10^{-12}～3.21×10^{-10}
		Pb	/～4.64×10^{-8}	/～5.53×10^{-8}	/～1.64×10^{-8}	/～1.95×10^{-8}
		Zn	/～2.29×10^{-9}	/～2.73×10^{-9}	/～7.67×10^{-11}	/～9.13×10^{-11}
		Fe	/～8.31×10^{-9}	/～9.90×10^{-9}	/～1.36×10^{-8}	/～1.62×10^{-8}
		Ni	3.85×10^{-11}～3.64×10^{-10}	4.59×10^{-11}～4.34×10^{-10}	2.04×10^{-11}～2.86×10^{-10}	2.43×10^{-11}～3.40×10^{-10}
		Mn	2.78×10^{-11}～2.31×10^{-8}	3.31×10^{-11}～2.76×10^{-8}	6.07×10^{-11}～1.44×10^{-8}	7.23×10^{-11}～1.72×10^{-8}
		Hg	/～1.54×10^{-9}	/～1.83×10^{-9}	/～1.64×10^{-9}	/～1.96×10^{-9}
Drinking Water	Carcinogenesis	As	/～4.40×10^{-7}	/～3.37×10^{-7}	1.57×10^{-8}～9.78×10^{-7}	1.21×10^{-8}～7.49×10^{-7}
		Cr	5.30×10^{-7}～2.38×10^{-6}	4.06×10^{-7}～1.83×10^{-6}	2.45×10^{-7}～2.38×10^{-6}	1.87×10^{-7}～1.83×10^{-6}
		Cd	/～1.01×10^{-6}	/～7.74×10^{-7}	/～2.42×10^{-8}	/～1.85×10^{-8}
	No-carcinogenesis	Al	2.35×10^{-12}～1.02×10^{-9}	1.80×10^{-12}～7.83×10^{-10}	1.92×10^{-12}～8.75×10^{-10}	1.47×10^{-12}～6.71×10^{-10}

Cu	/～3.62×10^{-12}	/～2.78×10^{-12}	2.31×10^{-14}～2.80×10^{-12}	1.77×10^{-14}～2.14×10^{-12}
Pb	/～3.21×10^{-12}	/～2.46×10^{-12}	/～1.13×10^{-12}	/～8.68×10^{-13}
Zn	/～2.14×10^{-10}	/～1.64×10^{-10}	/～7.15×10^{-12}	/～5.48×10^{-12}
Fe	/～2.87×10^{-11}	/～2.19×10^{-11}	/～4.70×10^{-11}	/～3.59×10^{-11}
Ni	7.39×10^{-14}～6.99×10^{-13}	5.66×10^{-14}～5.35×10^{-13}	3.92×10^{-14}～5.48×10^{-13}	3.00×10^{-14}～4.20×10^{-13}
Mn	3.68×10^{-13}～3.07×10^{-10}	2.82×10^{-13}～2.35×10^{-10}	8.04×10^{-13}～1.91×10^{-10}	6.16×10^{-13}～1.46×10^{-10}
Hg	/～1.43×10^{-11}	/～1.10^{-11}	/～1.53×10^{-11}	/～1.17×10^{-11}

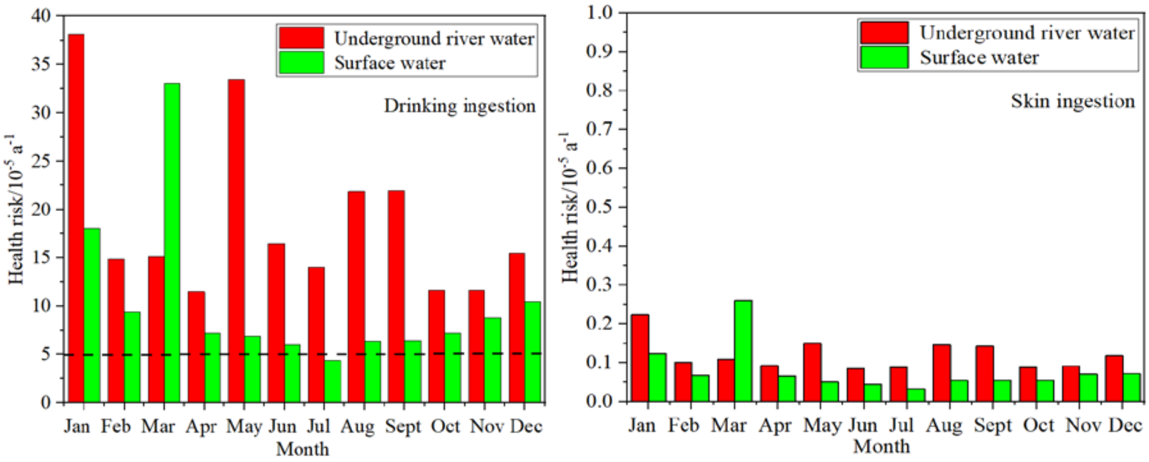
“/”means no calculation results.

Fig 2 and **Fig 3** show the changes of maximum total health risk values in different months for adults and children exposed to metal elements in the water throughout the year from 2021 to 2022, the Figs indicated that the maximum health risk values for adults and children caused by skin penetration and drinking presents are in the order of January > May > September > August > June > December > March > February > July > November > October > April in groundwater and March > January > December > February > November > April > October > May > September > August > June > July in surface water. Except for July, the maximum health risks values of other months for adults and children exposed to metal elements in the water by drinking were all higher than 5.0×10^{-5}.a^{-1}. However, those exposed to skin penetration were lower than 5.0×10^{-6}.a^{-1} and less than an order of magnitude below the maximum acceptable level. Therefore, it is necessary to treat carinogenic metal elements Cr, Cd and As when using the surface and groundwater water of Nandong Underground River Watershed as drinking water resource.



(**a**) (**b**)

Figure 2. Maximum health risks monthly exposure to metal elements from different water types by drinking and skin penetration for adults: **(a)** Drinking ingestion;**(b)** Skin ingestion.



(a) (b)

Figure 3. Maximum health risks monthly exposure to metal elements from different water types by drinking and skin penetration for children: **(a)** Drinking ingestion;**(b)** Skin ingestion.

Integration health risk studies of adults and children exposed to metal elements in the water in China, we found that health risks caused by water in most areas are mainly come from carinogenic metal elements, especially Cr in the water [21, 28, 29, 41]. In our study, we found that the mainly source of health risk for local residents exposed to metal elements in the water of Nandong Underground River Watershed is also Cr, followed by Cd and As. This is mainly related to the chemical carinogenic slope factor of carinogenic metal elements was higher than reference dose for average daily intake of no-carinogenic metal elements. It also reflects that carinogenic metal elements bring more toxicity to the human body. It is worth noting that, we used health risk assessment model recommended by USEPA (the United States Environmental Protection Agency) to calculate health risk of water in our study, the parameters used in this study were international unification, and it is not necessarily consistent with the true situation of the local residents of Yunnan Province [44]. Meanwhile, the universality of expose parameters in health risk assessment model does not take into account the individual differences. Furthermore, inhomogeneity of the metal concentration in the water can lead to they have spatial and temporal differences and causes the uncertainty in the evaluation results [29].

5. Summary and Conclusions

In this study, we collected 84 water samples (48 surface water samples and 36 underground water samples) and assessed the water quality in Nandong Underground River Watershed in terms of 11 common heavy metals based on Health risk assessment (HRA) model to evaluate the potential health risks for humans. The main conclusions are as follows.

The order of heavy metal concentrations in the water of Nandong Underground River Watershed was Fe> Al >Mn >Zn> As >Cd >Pb >Cr> Ni> Cu >Hg. The maximum concentrations of Hg, Fe, Al and Mn present exceed the standard many times (higher than 20%) and the highest value reached 26.37 times. Consequently, these four elements should be as the focus when managing the water quality in Nandong Underground River Watershed.

According to the result of HRA model, The health risks for local residents exposed to metal elements in the water of NURW mainly from carcinogenic risk (10^{-6}～10^{-4} a^{-1}) through drinking way. The health risk of heavy metals exposed to children through drinking way was much higher than adults, and the main contributing factors that can cause the risk of cancer were in the order of Cr > Cd > As in groundwater and Cr > As > Cd in surface water. Therefore, it is necessary to control these three metal elements before drinking to ensure health safety.

Many metals elements show significant positive correlations ($p<0.01$= between each other. The results of correlation analysis indicate that most of these metal elements have certain similarity material source and migration transformation, while Hg has distinguished on original source and migration transformation sharply from Cr and Ni elements since they have significant negative correlations with each other.

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